

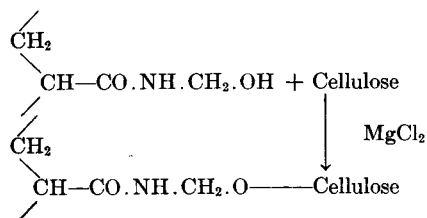
### Crosslinking of Cellulose Modified with Polyacrylonitrile

Recently Kamogawa and Sekiya<sup>1</sup> and Gardon<sup>2</sup> reported studies of the crosslinking of cotton fabrics by using acrylamide as starting substance. The former polymerized acrylamide in cotton fabrics and gave it a secondary after-treatment with various reactive compounds such as formalin and adipamide; the methylolated product was then crosslinked with cellulose by the usual acid curing treatment. The latter followed a reverse procedure, that of crosslinking *N*-methylol acrylamide with cellulose; i.e., the methylolated acrylamide was first made to react with cotton with a mild acid catalyst and then was cured. This was then crosslinked with cellulose by the use of ammonium persulfate or potassium hydroxide, to bring about the reaction of the vinyl double bonds with cellulose hydroxyls.

In both cases there was reported a considerable improvement in the wrinkle recovery of the treated fabrics.

In our studies on the polymerization of acrylonitrile in cotton fabrics, crosslinking and improved fabric crease recovery were obtained through treatments essentially similar to those described above.

The nitrile group in polyacrylonitrile was first saponified to the amide by reaction with sodium hydroxide of varying concentrations.<sup>3</sup> This then reacted with formaldehyde (30%) at 9–9.5 pH, to give the methylol which is known to react with cellulose under an acid curing treatment. It is interesting to note that, although the reaction of the polymer chain with cellulose can occur at one end only, viz.,



the treated fabrics exhibit considerable improvement in wet crease recovery, indicating the presence of polymer crosslinking with cellulose.

This would therefore substantiate the hypothesis that, during the polymerization process, the polymer is grafted to cellulose at the vinyl double bonds. Such a graft, when modified and made to react further with cellulose by the above method, would produce crosslinks and improve the wrinkle recovery of the fabrics.

Details of this work, together with other evidence supporting graft formation of polyacrylonitrile with cellulose will be published shortly.

#### References

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3. Schildknecht, C. E., *Vinyl and Related Polymers*, Wiley, New York, 1952, pp. 272.

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### Adhesion Properties of Nylons

A study was undertaken to evaluate the characteristics of nylon adhesion to metal surfaces. These polymers were selected because they can be applied as hot-melt adhesives and are, therefore, one-component systems. Furthermore, they contain a single type of active group, the amide group. Adhesion strengths of nylon-metal joints were determined and the results were analyzed in the light of adhesion fundamentals. In this work, a series of linear nylons was studied and the role that mechanical properties of polymers play in dictating adhesive joint strength was investigated.

Three different adhesion tests—tensile, lap shear and impact—were used in these experiments, giving a better overall performance rating of the adhesive and enabled an objective examination of the results to be made. The tensile tests were a modification of the ASTM C297-52T procedure. However, a circular instead of a square contact area was used to eliminate corner effects. Lap shear strengths were obtained by rupturing (in tension) joints made by melting the polymer between two metal bars (4 in. × 1/2 in. × 1/4 in.) at 1/2 in. overlap. A test resembling the IZOD impact test was employed to obtain impact strengths. In all tests, the contact surfaces were first cleaned and smoothed with Carborundum silicon carbide paper (#400/w) on a flat surface. They were washed with acetone and water, and then given a chemical conditioning treatment. The aluminum and steel surfaces were treated as described by Black and Blomquist.<sup>1</sup> The copper surfaces were dipped in concentrated nitric acid and immediately washed with water. The polymers were then melted onto the blocks, and while still fluid were pressed together with minimum contact pressure, to insure proper spreading and joint formation.

Results of the adhesion tests are presented in Table I; data for polyethylene are included for comparison. Generally, with the exception of Nylon 48, adhesion strengths vary according to the amide content. Table I also lists some mechanical properties of the polymers. Comparison shows that a clear correlation exists between bulk mechanical strength of the polymeric adhesive and adhesive strength. These data confirm the known fact that rheological properties of adhesive materials are most important in dictating ultimate joint strengths of adhesives.<sup>2</sup> However, contrary to expectation, the ruptured joints were observed to exhibit partly boundary and partly cohesive failure. What must be assumed in this case, since it is known that the amide groups of nylon are capable of influencing both interfacial and bulk properties simultaneously, is that the boundary layer is initially sufficiently strong to support an external force. When a breaking stress is applied to the joint, the failure crack notably initiates in the bulk of the adhesive polymer and thus the adhesion strength reflects the bulk polymer strength. The rupture course proceeds in any direction by a tearing or peeling mechanism. The failure crack may then be expected to propagate along the metal-polymer boundary as well as in the layer of polymer. This latter step would be rapid and require little energy. This hypothesis suggests that a "threshold" of interfacial boundary strength may exist, by which is meant that, if the mechanical strength of the boundary layer is above that of the bulk polymer, interfacial properties would not be expected to influence the strength behavior of the composite joints. Similar views of adhesion are held by Bikerman.<sup>3</sup>